PROCESS FOR PREPARING A SUBSTANTIALLY TRANSPARENT CONDUCTIVE LAYER CONFIGURATION

This application claims the benefit of U.S. Provisional Application No. 60/411,556 filed September 18, 2002, which is incorporated by reference. In addition, this application claims the benefit of International Application No. PCT/EP 02/09429 filed August 22, 2002, which is also incorporated by reference.

Field of the invention

The present invention relates to a process for producing a substantially transparent conductive layer configuration.

Background of the invention.

In many applications there is a requirement for inexpensive transparent conducting layers, but a busbar will be also required for some of the (large area) applications. Highly conductive (non-transparent) patterns can be made by screen-printing conducting pastes such as silver or carbon black pastes. Vacuum evaporation of metals through shadow masks is another method. Yet another method makes use of homogeneous conductive metallized surfaces which can be patterned by use of photoresist technology in combination with a metal etching agent. Photographic films can, under certain conditions, be used for making electrically conductive silver "images".

US 3,664,837 describes the use of light sensitive evaporated silver halide film which upon exposure and after development results in conductive images. DE 1,938,373 describes a photographic method for producing conducting paths, resistances and capacitors for microcircuits starting from coated silver halide emulsions. US 3,600,185 describes the production of electrically conductive patterns by means of diffusion transfer techniques.

DE-A 1938373 discloses a process for manufacturing passive elements such as resistances, capacitors, RC-components and conductive track by negative development with the aid of a light-sensitive multilayer silver halide material, comprising a non-conductive support and two different spectrally sensitized gelatin-containing silver chlorobromide emulsions one above another with a gelatin/silver ratio of at least 1:3, which are separated by a

photographic bath permeable dielectric layer, which are developed in the presence of a known development booster.

Combinations of a transparent polymer-based conductor and a high conductive (non-transparent) pattern are described in some
5 publications.

DE-A 196 27 071 discloses an electroluminescent configuration, which contains hole and/or electron injecting layers, wherein the polymeric organic conductor is selected from the group of polyfurans, polypyrroles, polyanilines, polythiophenes and
10 polypyridines. DE-A 196 27 071 also discloses the use of poly(3,4-ethylenedioxythiophene) as a charge-injection layer on transparent metallic electrodes such as ITO (indium-tin oxide) and that the following materials are suitable as transparent and conductive materials: a) metal oxides e.g. ITO, tin oxide etc.; b) semi-
15 transparent metal films e.g. Au, Pt, Ag, Cu etc. The latter being applied by vacuum techniques.

EP-A 510 541 discloses an organic electroluminescent device having an anode, an organic hole injection transport layer, an organic luminescent layer and a cathode formed sequentially in this
20 order, wherein the organic hole injection transport layer contains a metal complex and/or a metal salt of an aromatic carboxylic acid. EP-A 510 541 further discloses that the conductive layers used in such devices may have a multi-layer structure by depositing different types of conductive materials selected from a metal, e.g.
25 Al, Au, Ag, Ni, Pd or Te, a metal oxide, carbon black or a conductive resin such as poly(3-methylthiophene), but no specific combinations are exemplified.

US 5,447,824 discloses a method of manufacturing a pattern of an electrically conductive polymer on a substrate surface, said method
30 comprising: a) forming a liquid layer on a surface of said substrate from a solution containing a material capable of forming said electrically conductive polymer upon being heated, e.g. 3,4-ethylenedioxythiophene, an oxidizing agent and a base, b) exposing said liquid layer to patterned radiation, and c) heating said layer
35 thereby forming a pattern of an electrically conductive polymer, said conductive polymer being formed in unexposed areas and a non-conductive polymer being formed in the exposed areas of the layer. The galvanic provision of the conductive polymer pattern with a metal layer, e.g. silver, copper, nickel or chromium, is also
40 disclosed in US 5,447,824.

WO 98/54767 discloses a conductive layer system, particularly for a transparent or semi-transparent electrode or

electroluminescent configuration, comprising at least two layers, characterized in that the first layer contains an organic or organometallic electrically conductive polymer, which is transparent or semi-transparent in the visible range of the electromagnetic

5 spectrum, e.g. a polymer selected from the group consisting of polythiophene, polypyrrole, polyaniline, polyacetylene or their optionally substituted derivatives and the second layer contains at least one electrically conductive inorganic compound or a metal or an appropriately doped semi-metal e.g. a material selected from the

10 group consisting of Cu, Ag, Au, Pt, Pd, Fe, Cr, Sn, Al or their alloys or conductive carbon. In a preferred embodiment the second layer is a conductive pattern formed by an open grid structure, preferably with a 5-500 μm grid so that it cannot be perceived by the human eye. Invention example 2 discloses a poly(3,4-

15 ethylenedioxythiophene) [PEDOT]/poly(styrene sulphonate) [PSS] layer with a surface resistivity of 1500 Ω/square to which conducting tracks of Leitsilber™ (a silver particle dispersion) ca. 2 mm wide had been applied by a printing technique.

The layer configuration disclosed in Example 2 of WO 98/54767

20 has the disadvantages of the grid of Leitsilber™ requiring a thickness of 5 to 10 μm to realize layers with a surface resistance of 0.5 to 1 Ω/square, which means that the surface of the configuration will have a certain roughness which will limit its applications, making it difficult to apply a thin, e.g. 100 nm,

25 functional layer. Furthermore, an aqueous PEDOT/PSS dispersion would not wet such a Leitsilber™ grid and hence a usable multilayer conductive configuration would not result.

Furthermore, such a reversed order: first a conductive metal grid and then a conductive transparent polymeric layer will

30 certainly be of more importance in LED devices and thin film photovoltaic devices, in which the transparent polymeric electrode performs as a hole-injecting layer.

Aspects of the invention.

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It is therefore an aspect of the present invention to provide a process for preparing a multilayer electrode configuration comprising a conductive polymer layer and a conductive metal layer in which it is possible to realize either the conductive polymer

40 layer or the conductive metal layer nearer the support.

It is a further aspect of the present invention to provide a process for preparing a multilayer electrode configuration

comprising a conductive polymer layer and a conductive metal layer in which it is possible to apply a functional layer system.

It is also an aspect of the present invention to prevent ion migration from the conductive electrode.

5   Further aspects and advantages of the invention will become apparent from the description hereinafter.

Summary of the invention.

10   It has been surprisingly found that by preparing the silver grid in a multilayer configuration comprising a first layer containing an intrinsically conductive polymer, such as PEDOT/PSS, and a second layer which is a silver pattern using a photographic process enables a configuration to be realized with the PEDOT/PSS layer or the

15   silver pattern outermost such that functional layers can be readily applied to its outermost layer.

Aspects of the present invention are realized by a process for preparing a substantially transparent conductive layer configuration on a support, the layer configuration comprising in any order at

20   least a first layer containing an intrinsically conductive polymer and a second layer consisting of a non-continuous layer of conductive silver, the process comprising the step of: preparing the second layer by a photographic process.

Aspects of the present invention are also realized by a layer

25   configuration obtainable by the process, according to the present invention, wherein the layer configuration further contains a 1-phenyl-5-mercapto-tetrazole compound in which the phenyl group is substituted with at least one electron accepting group.

Aspects of the present invention are also realized by a light

30   emitting diode comprising a layer configuration prepared according to the above-mentioned process.

Aspects of the present invention are also realized by a photovoltaic device comprising a layer configuration prepared according to the above-mentioned process.

35   Aspects of the present invention are also realized by a transistor comprising a layer configuration prepared according to the above-mentioned process.

Aspects of the present invention are also realized by an electroluminescent device comprising a layer configuration prepared

40   according to the above-mentioned process.

Preferred embodiments are disclosed in the dependent claims.

Detailed description of the invention.

Figure 1 shows four silver patterns, pattern (a) representing a continuous silver layer 3 x 3 cm^2 in area, pattern (b) representing
5 a regular strip pattern, the parallel strips being 10 mm apart and having a width of 1 mm; pattern (c) representing a regular strip pattern, the parallel strips being 5 mm apart and having a width of 150 µm; and pattern (d) representing no silver development.

10 Figure 2 shows side (upper) and top (lower) views of a sequential process for building up a module with a separate photovoltaic cell, two serially connected photovoltaic cells and three serially connected photovoltaic cells using a six step process in which: A = a subbed support; B = a gelatin layer; C = a palladium sulphide
15 nucleation layer; D = a conductive silver pattern; E = a highly conductive PEDOT/PSS-layer; F = a shunt resistance hindering layer; G = a photovoltaic blend; and H = a lithium fluoride/aluminium electrode. In step 1 in which the subbed surface of a subbed poly(ethylene terephthalate) film A [the subbing layer represented
20 by hatching] is coated with a gelatin layer B; step 2 in which a palladium sulfide nucleation layer C is applied to the gelatin layer B; step 3 in which a diffusion transfer process is carried out in which a conductive silver pattern D is produced; step 4 in which the conductive silver pattern D is coated with a highly conductive
25 PEDOT/PSS-layer E by e.g. screen printing, and optionally additionally with a shunt resistance hindering layer F, e.g. a PEDOT/PSS layer or a PEDOT-S/polycationic or polyanionic polymer with a higher surface resistance; step 5 in which layer E or F is coated with a photovoltaic blend, e.g. a blend of MDMO-PPV/PCBM G,
30 by e.g. curtain coating, spin-coating or screen printing; and step 6 in which layer G is coated with a non-continuous lithium fluoride/aluminium layer forming a top electrode H.

Definitions

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The term alkyl means all variants possible for each number of carbon atoms in the alkyl group i.e. for three carbon atoms: n-propyl and isopropyl; for four carbon atoms: n-butyl, isobutyl and tertiary-butyl; for five carbon atoms: n-pentyl, 1,1-dimethyl-
40 propyl, 2,2-dimethylpropyl and 2-methyl-butyl etc.

The term aqueous for the purposes of the present invention means containing at least 60% by volume of water, preferably at least 80%

by volume of water, and optionally containing water-miscible organic solvents such as alcohols e.g. methanol, ethanol, 2-propanol, butanol, iso-amyl alcohol, octanol, cetyl alcohol etc.; glycols e.g. ethylene glycol; glycerine; N-methyl pyrrolidone; methoxypropanol;
5 and ketones e.g. 2-propanone and 2-butanone etc.

The term "support" means a "self-supporting material" so as to distinguish it from a "layer" which may be coated on a support, but which is itself not self-supporting. It also includes any treatment necessary for, or layer applied to aid, adhesion to the support.
10 The term continuous layer refers to a layer in a single plane covering the whole area of the support and not necessarily in direct contact with the support.

The term non-continuous layer refers to a layer in a single plane not covering the whole area of the support and not necessarily
15 in direct contact with the support.

The term coating in used as a generic term including all means of applying a layer including all techniques for producing continuous layers, such as curtain coating, doctor-blade coating etc., and all techniques for producing non-continuous layers such as
20 screen printing, ink jet printing, flexographic printing, and techniques for producing continuous layers

The term intrinsically conductive polymer means organic polymers which have (poly)-conjugated π-electron systems (e.g. double bonds, aromatic or heteroaromatic rings or triple bonds) and
25 whose conductive properties are not influenced by environmental factors such as relative humidity.

The term "conductive" is related to the electric resistance of the material. The electric resistance of a layer is generally expressed in terms of surface resistance R_s (unit Ω; often specified
30 as Ω/square). Alternatively, the conductivity may be expressed in terms of volume resistivity $R_v = R_s \cdot d$, wherein d is the thickness of the layer, volume conductivity $k_v = 1/R_v$ [unit: S(iemens)/cm] or surface conductance $k_s = 1/R_s$ [unit: S(iemens).square].

The term photographic refers to any photochemical process
35 particularly those based on silver halide processes.

The term silver salt diffusion transfer process refers to a process developed independently by A. Rott [GB 614,155 and Sci. Photogr., (2)13, 151 (1942)]and E. Weyde [DE 973,769] and described by G. I. P. Levenson in Chapter 16 of "The Theory of the
40 Photographic Process Fourth Edition", edited by T. H. James, pages 466 to 480, Eastman Kodak Company, Rochester (1977).

The term substantially transparent means that the integral transmission of visible light is above 40% of the incident light normal to the layer configuration of the present invention i.e. the layer had an overall optical density of less than 0.40, although

5 local transmission of visible light though the lines of the silver pattern may be well below 10% of the incident light normal to the layer configuration of the present invention i.e. well above an optical density of 1.0.

The abbreviation PEDOT represents poly(3,4-ethylenedioxy-

10 thiophene).

The abbreviation PSS represents poly(styrene sulphonic acid) or poly(styrenesulphonate).

The abbreviation PEDOT-S represents poly[4-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-2-ylmethoxy)-butane-1-sulphonic acid].

15

Process for preparing a layer configuration

Aspects of the present invention are realized by a process for preparing a substantially transparent conductive layer configuration

20 on a support, the layer configuration comprising in any order at least a first layer containing an intrinsically conductive polymer and a second layer consisting of a non-continuous layer of conductive silver, the process comprising the step of: preparing the second layer by a photographic process.

25 According to a first embodiment of the process, according to the present invention the process further comprises coating the first layer prior to preparing the second layer by a photographic process.

According to a second embodiment of the process, according to the present invention, the photographic process comprises the steps

30 of: coating the support with a layer containing silver halide and gelatin with a weight ratio of gelatin to silver halide in the range of 0.05 to 0.3, image-wise exposing the silver halide-containing layer, and developing the exposed silver halide-containing layer to produce the second layer.

35 According to a third embodiment of the process, according to the present invention, the process comprises the steps of: coating the support with the first layer, coating the first layer with a layer containing silver halide and gelatin with a weight ratio of gelatin to silver halide in the range of 0.05 to 0.3, image-wise exposing

40 the silver halide-containing layer, and developing the exposed silver halide-containing layer to produce the second layer.

According to a fourth embodiment of the process, according to the present invention, the process comprises the steps of: coating the support a layer containing silver halide and gelatin with a weight ratio of gelatin to silver halide in the range of 0.05 to 0.3, coating the silver halide-containing layer with the first layer, image-wise exposing the silver halide-containing layer, and developing the exposed silver halide-containing layer to produce the second layer.

According to a fifth embodiment of the process, according to the present invention, the process comprises the steps of: coating the support with a layer containing silver halide and gelatin with a weight ratio of gelatin to silver halide in the range of 0.05 to 0.3, image-wise exposing the silver halide-containing layer, developing the exposed silver halide-containing layer to produce the second layer, and coating the second layer with the first layer.

According to a sixth embodiment of the process, according to the present invention, the photographic process comprises the steps of: coating the support with a non-continuous layer of a nucleation agent; producing the second layer on the non-continuous nucleation layer using silver salt diffusion transfer.

According to a seventh embodiment of the process, according to the present invention, the photographic process comprises the steps of: coating the support with the first layer, coating the first layer with a layer of a nucleation agent; producing a non-continuous silver layer on the nucleation layer using silver salt diffusion transfer.

According to an eighth embodiment of the process, according to the present invention, the photographic process comprises the steps of: coating the support with a non-continuous layer of a nucleation agent; coating the non-continuous layer of a nucleation agent with the first layer; and producing a non-continuous silver layer on the non-continuous nucleation layer using silver salt diffusion transfer.

According to a ninth embodiment of the process, according to the present invention, the photographic process comprises the steps of: coating the support with a non-continuous layer of palladium sulphide, e.g. palladium sulphide nano-particles, as nucleation agent; producing a non-continuous silver layer on the non-continuous nucleation layer using silver salt diffusion transfer.

According to a tenth embodiment of the process, according to the present invention, the process comprises the steps of: coating the support with a non-continuous layer of a nucleation agent; producing
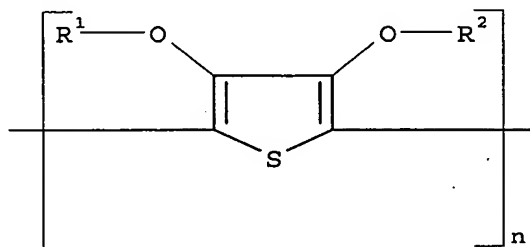
the second layer on the non-continuous nucleation layer using silver salt diffusion transfer; and coating the second layer with the first layer.

5   According to an eleventh embodiment of the process, according to the present invention, the first layer is applied by a printing process.

Intrinsically conductive polymer

10   · The intrinsically conductive polymers used in the present invention can be any intrinsically conductive polymer known in the art e.g. polyacetylene, polypyrrole, polyaniline, polythiophene, etc. Details about suitable intrinsically conductive polymers can be found in textbooks, such as "Advances in Synthetic Metals", ed.
15   P. Bernier, S. Lefrant, and G. Bidan, Elsevier, 1999; "Intrinsically Conducting Polymers: An Emerging Technology", Kluwer (1993); "Conducting Polymer Fundamentals and Applications, A Practical Approach", P. Chandrasekhar, Kluwer, 1999; and "Handbook of Organic Conducting Molecules and Polymers", Ed. Walwa, Vol. 1-4, Marcel
20   Dekker Inc. (1997).

According to a twelfth embodiment of the process, according to the present invention, the intrinsically conductive polymer contains structural units represented by formula (I):

$$\left[\begin{array}{c} R^1\!\!-\!\!O \qquad\qquad O\!\!-\!\!R^2 \\[2pt] \diagdown\ \diagup \\ \| \qquad \| \\ \diagup\ S\ \diagdown \end{array}\right]_n$$

(I)

25   in which, each of R^1 and R^2 independently represents hydrogen or a C_{1-4} alkyl group or together represent an optionally substituted C_{1-4} alkylene group or a cycloalkylene group.

According to a thirteenth embodiment of the process, according to the present invention, the intrinsically conductive polymer is a
30   polymer or copolymer of a 3,4-dialkoxythiophene in which the two alkoxy groups together represent an optionally substituted oxy-alkylene-oxy bridge.

According to a fourteenth embodiment of the process, according to the present invention, the intrinsically conductive polymer is a
35   polymer or copolymer of a 3,4-dialkoxy-thiophenes in which the two alkoxy groups together represent an optionally substituted oxy-

alkylene-oxy bridge and is selected from the group consisting of:
poly(3,4-methylenedioxythiophene), poly(3,4-methylenedioxy-
thiophene) derivatives, poly(3,4-ethylenedioxythiophene), poly(3,4-
ethylene-dioxythiophene) derivatives, poly(3,4-propylenedioxy-
5 thiophene), poly(3,4-propylenedioxy-thiophene) derivatives,
poly(3,4-butylene-dioxythiophene) and poly(3,4-butylenedioxy-
thiophene) derivatives and copolymers thereof.

    According to a fifteenth embodiment of the process, according to
the present invention, the intrinsically conductive polymer is a
10 polymer or copolymer of a 3,4-dialkoxy-thiophenes in which the two
alkoxy groups together represent an optionally substituted oxy-
alkylene-oxy bridge and the substituents for the oxy-alkylene-oxy
bridge are alkyl, alkoxy, alkyloxyalkyl, carboxy, alkylsulfonato and
carboxy ester groups.

15   According to a sixteenth embodiment of the process, according to
the present invention, the intrinsically conductive polymer is a
polymer or copolymer of a 3,4-dialkoxy-thiophenes in which the two
alkoxy groups together represent an optionally substituted oxy-
alkylene-oxy bridge and the two alkoxy groups together represent an
20 optionally substituted oxy-alkylene-oxy bridge which is a 1,2-
ethylene group, an optionally alkyl-substituted methylene group, an
optionally C1-12 alkyl- or phenyl-substituted 1,2-ethylene group, a
1,3-propylene group or a 1,2-cyclohexylene group.

    Such polymers are disclosed in Handbook of Oligo- and
25 Polythiophenes Edited by D. Fichou, Wiley-VCH, Weinheim (1999); by
L. Groenendaal et al. in Advanced Materials, volume 12, pages 481-
494 (2000); L. J. Kloeppner et al. in Polymer Preprints, volume
40(2), page 792 (1999); P. Schottland et al. in Synthetic Metals,
volume 101, pages 7-8 (1999); and D. M. Welsh et al. in Polymer
30 Preprints, volume 38(2), page 320 (1997).

    Organic polymer containing structural units according to formula
(I) can be polymerized chemically or electrochemically. Chemical
polymerization can be carried out oxidatively or reductively. The
oxidation agents used for the oxidative polymerisation of pyrrole,
35 such as described for example in J. Amer. Chem. Soc., vol. 85, pages
454-458 (1963) and J. Polymer Science Part A Polymer Chemistry, vol.
26, pages 1287-1294 (1988), can be utilized for the oxidative
polymerization of thiophenes. According to a seventh embodiment of
the present invention, the inexpensive and easily accessible
40 oxidation agents such as iron(III) salts such as $FeCl_3$, the
iron(III) salts of organic acids, e.g. $Fe(OTs)_3$, H_2O_2, $K_2Cr_2O_7$,

alkali and ammonium persulphates, alkali perborates and potassium permanganate are used in the oxidative polymerization.

Theoretically the oxidative polymerization of thiophenes requires 2.25 equivalents of oxidation agent per mole thiophene of

5 formula (I) [see e.g. J. Polymer Science Part A Polymer Chemistry, vol. 26, pages 1287-1294 (1988)]. In practice an excess of 0.1 to 2 equivalents of oxidation agent is used per polymerizable unit. The use of persulphates and iron(III) salts has the great technical advantage that they do not act corrosively. Furthermore, in the

10 presence of particular additives oxidative polymerization of the thiophene compounds according to formula (I) proceeds so slowly that the thiophenes and oxidation agent can be brought together as a solution or paste and applied to the substrate to be treated. After application of such solutions or pastes the oxidative polymerization

15 can be accelerated by heating the coated substrate as disclosed in US 6,001,281 and WO 00/14139 herein incorporated by reference.

Reductive polymerization can be performed using the Stille (organotin) or Suzuki (organoboron) routes described in 2002 by Appperloo et al. in Chem. Eur. Journal, volume 8, pages 2384-2396,

20 and as disclosed in 2001 in Tetrahedron Letters, volume 42, pages 155-157 and in 1998 in Macromolecules, volume 31, pages 2047-2056 respectively or with nickel complexes as disclosed in 1999 in Bull. Chem. Soc. Japan, volume 72, page 621 and in 1998 in Advanced Materials, volume 10, pages 93-116.

25

1-Phenyl-5-mercapto-tetrazole compound substituted with at least one electron accepting group

Aspects of the present invention are also realized by a layer

30 configuration obtainable by the process, according to the present invention, wherein the layer configuration further contains a 1-phenyl-5-mercapto-tetrazole compound in which the phenyl group is substituted with at least one electron accepting group.

According to a first embodiment of the layer configuration

35 conducting layer obtainable by the process, according to the present invention, the electron accepting group is selected from the group consisting of chloride, fluoride, cyano, sulfonyl, nitro, acid amido and acylamino groups.

According to a second embodiment of the layer configuration

40 obtainable by the process, according to the present invention, the 1-phenyl-5-mercapto-tetrazole compound in which the phenyl group is substituted with at least one electron accepting group is selected
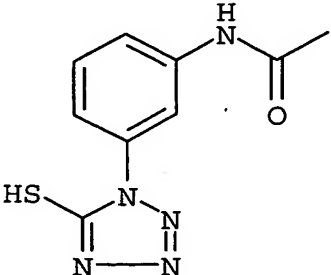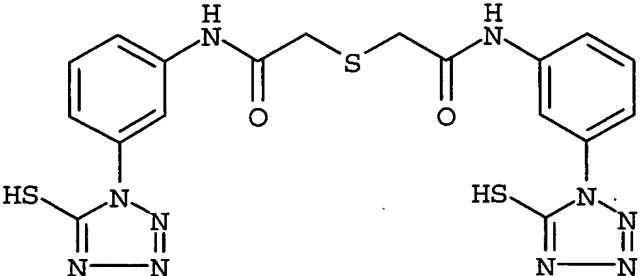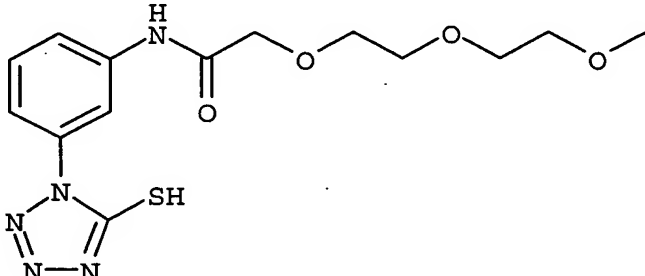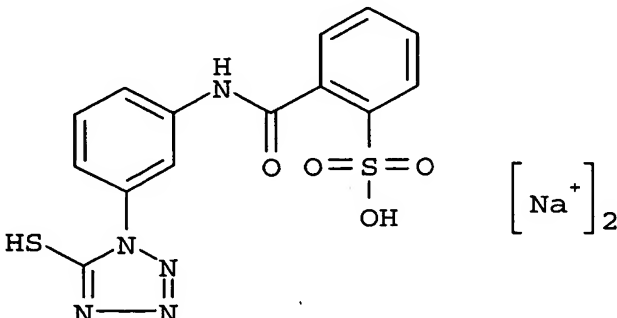
from the group consisting of: 1-(3',4'-dichlorophenyl)-5-mercapto-
tetrazole,

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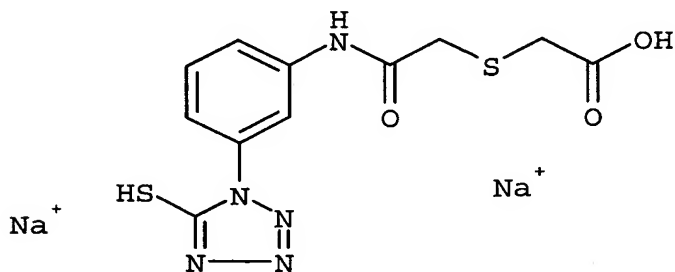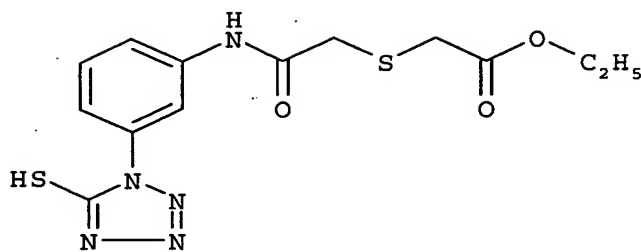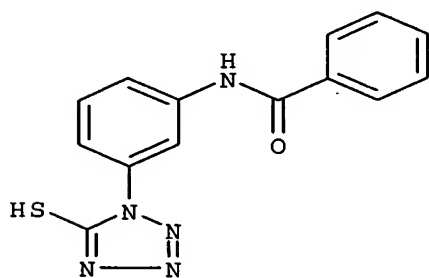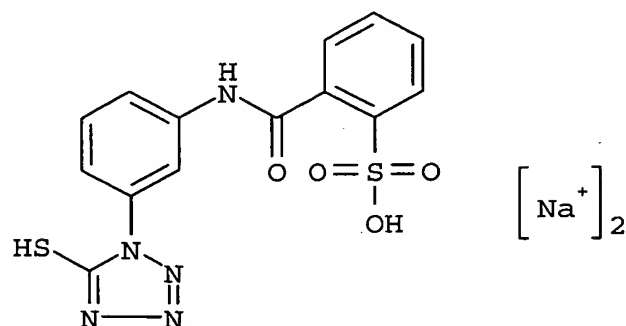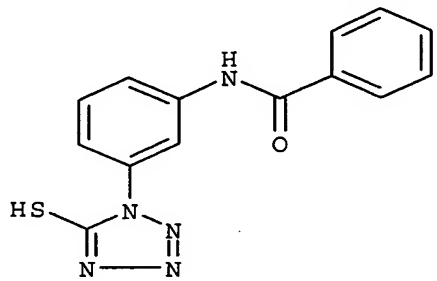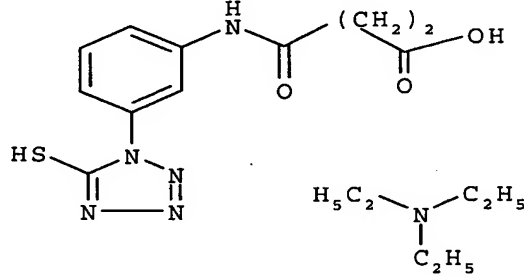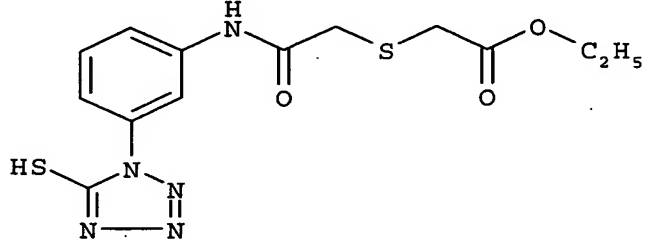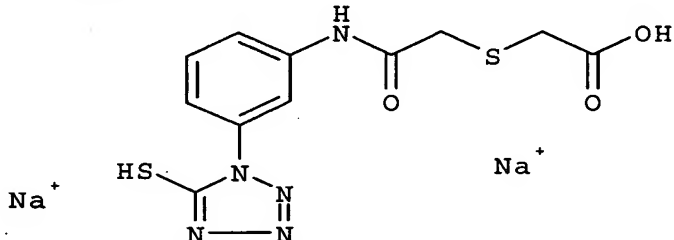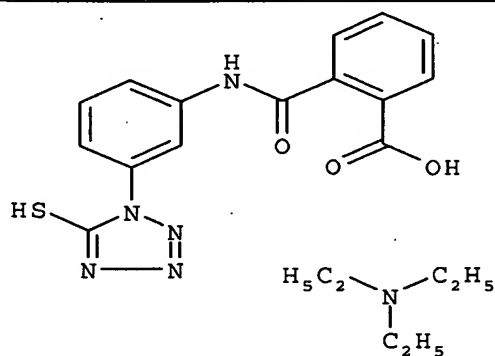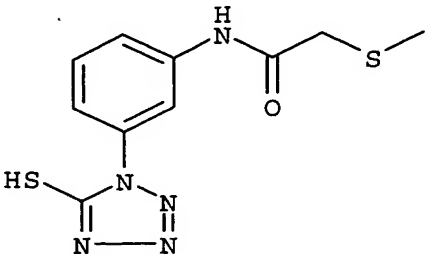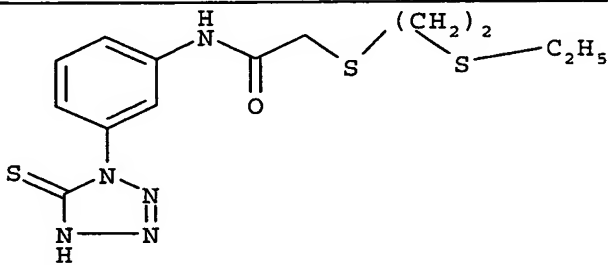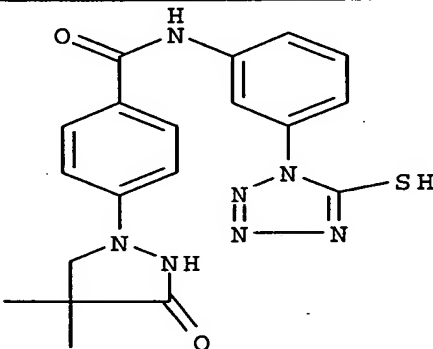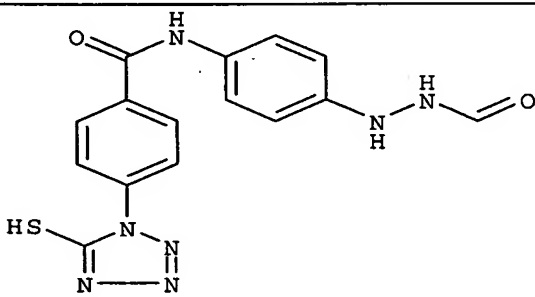
and
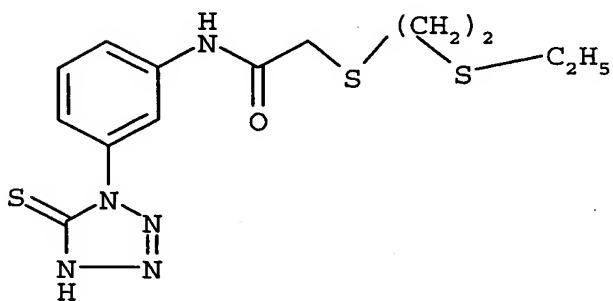
Suitable 1-phenyl-5-mercapto-tetrazole compounds with
substituted phenyl groups [PMT], according to the present invention,
10 include:

	Structural formula	
PMT01		1-(3',4'-dichlorophenyl)-5-mercapto-tetrazole
PMT02		1-(3'-acetylamino-phenyl)-5-mercapto-tetrazole
PMT03		
PMT04		
PMT05		

PMT06		1-(3'-benzoylamino-phenyl)-5-mercapto-tetrazole
PMT07		
PMT08		
PMT09		
PMT10		

PMT11	(structure: phenyl ring with N–H, C(=O)CH₂–S–CH₃ amide; HS–C linked to tetrazole ring N–N–N)	
PMT12	(structure: phenyl ring with N–H, C(=O)CH₂–S–(CH₂)₂–S–C₂H₅; S=C tetrazole ring with N–H)	
PMT13	(structure: benzamide O=C–N–H to phenyl, triazole with SH, N–NH ring with O and methyls)	
PMT14	(structure: benzamide O=C–N–H to phenyl, N–H–N–H–C(=O) formyl hydrazide; HS–tetrazole)	

Printing inks containing an intrinsically conductive polymer

According to a seventeenth embodiment of the process, according
5 to the present invention, the first layer is applied by a printing
process using an ink or paste containing an intrinsically conductive
polymer.

A printing ink or paste containing between 0.08 and 3.0% by
weight of polymer or copolymer of a 3,4-dialkoxythiophene in which
10 the two alkoxy groups may be the same or different or together
represent an optionally substituted oxy-alkylene-oxy bridge, a
polyanion and non-aqueous solvent can be prepared from a dispersion

of the polymer or copolymer of (3,4-dialkoxythiophene) and the polyanion in water by a method comprising the steps of: i) mixing at least one non-aqueous solvent with the aqueous dispersion of the polymer or copolymer of (3,4-dialkoxythiophene) and the polyanion;
5 and ii) evaporating water from the mixture prepared in step i) until the content of water therein is reduced by at least 65% by weight.

Surfactants

10   According to a third embodiment of the layer configuration, according to the present invention, the layer configuration further contains a surfactant.

      According to a fourth embodiment of the layer configuration, according to the present invention, the layer configuration further
15 contains a non-ionic surfactant e.g. ethoxylated/fluoro-alkyl surfactants, polyethoxylated silicone surfactants, polysiloxane/polyether surfactants, ammonium salts of perfluoro-alkylcarboxylic acids, polyethoxylated surfactants and fluorine-containing surfactants.

20   Suitable non-ionic surfactants include:

Surfactant no. 01 = ZONYL™ FSN, a 40% by weight solution of $F(CF_2CF_2)_{1-9}CH_2CH_2O(CH_2CH_2O)_xH$ in a 50% by weight solution of isopropanol in water where x = 0 to about 25, from DuPont;

Surfactant no. 02 = ZONYL™ FSN-100: $F(CF_2CF_2)_{1-9}CH_2CH_2O(CH_2CH_2O)_xH$ where x = 0 to about 25, from DuPont;

Surfactant no. 03 = ZONYL™ FS300, a 40% by weight aqueous solution of a fluorinated surfactant, from DuPont;

Surfactant no. 04 = ZONYL™ FSO, a 50% by weight solution of a mixture of ethoxylated non-ionic fluoro-surfactant with the formula:
$F(CF_2CF_2)_{1-7}CH_2CH_2O(CH_2CH_2O)_yH$ where y = 0 to ca. 15 in a 50% by weight solution of ethylene glycol in water, from DuPont;

Surfactant no. 05 = ZONYL™ FSO-100, a mixture of ethoxylated non-ionic fluoro-surfactant from DuPont with the formula: $F(CF_2CF_2)_{1-7}CH_2CH_2O(CH_2CH_2O)_yH$ where y = 0 to ca. 15 from DuPont;

Surfactant no. 06 = Tegoglide™ 410, a polysiloxane-polymer copolymer surfactant, from Goldschmidt;

Surfactant no. 07 = Tegowet™, a polysiloxane-polyester copolymer

surfactant, from Goldschmidt;

Surfactant no. 08 = FLUORAD™FC431: $CF_3(CF_2)_7SO_2(C_2H_5)N-CH_2CO-(OCH_2CH_2)_nOH$ from 3M;

Surfactant no. 09 = FLUORAD™FC126, a mixture of the ammonium salts of perfluorocarboxylic acids, from 3M;

Surfactant no. 10 = Polyoxyethylene-10-lauryl ether

Surfactant no. 11 = FLUORAD™FC430, a 98.5% active fluoroaliphatic ester from 3M;

According to a fifth embodiment of the layer configuration, according to the present invention, the layer configuration further contains an anionic surfactant.

5   Suitable anionic surfactants include:

Surfactant no. 12 = ZONYL™ 7950, a fluorinated surfactant, from DuPont;

Surfactant no. 13 = ZONYL™ FSA, 25% by weight solution of $F(CF_2CF_2)_{1-9}CH_2CH_2SCH_2CH_2COOLi$ in a 50% by weight solution of isopropanol in water, from DuPont;

Surfactant no. 14 = ZONYL™ FSE, a 14% by weight solution of $[F(CF_2CF_2)_{1-7}CH_2CH_2O]_xP(O)(ONH_4)_y$ where x = 1 or 2; y = 2 or 1; and x + y = 3 in a 70% by weight aqueous ethylene glycol solution, from DuPont;

Surfactant no. 15 = ZONYL™ FSJ, a 40% by weight solution of a blend of $F(CF_2CF_2)_{1-7}CH_2CH_2O]_xP(O)(ONH_4)_y$ where x = 1 or 2; y = 2 or 1; and x + y = 3 with a hydrocarbon surfactant in 25% by weight solution of isopropanol in water, from DuPont;

Surfactant no. 16 = ZONYL™ FSP, a 35% by weight solution of $[F(CF_2CF_2)_{1-7}CH_2CH_2O]_xP(O)(ONH_4)_y$ where x = 1 or 2; y = 2 or 1 and x + y = 3 in 69.2% by weight solution of isopropanol in water, from DuPont;

Surfactant no. 17 = ZONYL™ UR: $[F(CF_2CF_2)_{1-7}CH_2CH_2O]_xP(O)(OH)_y$ where x = 1 or 2; y = 2 or 1 and x + y = 3, from DuPont;

Surfactant no. 18 = ZONYL™ TBS: a 33% by weight solution of $F(CF_2CF_2)_{3-8}CH_2CH_2SO_3H$ in a 4.5% by weight solution of acetic acid in water, from DuPont;

Surfactant no. 19 = ammonium salt of perfluoro-octanoic acid from 3M

Binder

According to a sixth embodiment of the layer configuration, according to the present invention, the layer configuration further contains a binder.

Crosslinking agent

According to a seventh embodiment of the layer configuration, according to the present invention, the layer configuration further contains a cross-linking agent.

Electroluminescent phosphors

According to an eighth embodiment of the layer configuration, according to the present invention, the layer configuration further comprises a layer of an electroluminescent phosphor.

According to a ninth embodiment of the layer configuration, according to the present invention, the layer configuration further comprises a layer of an electroluminescent phosphor, wherein the electroluminescent phosphor belongs to the class of II-VI semiconductors e.g. ZnS, or is a combination of group II elements with oxidic anions, the most common being silicates, phosphates, carbonates, germanates, stannates, borates, vanadates, tungstates and oxysulphates. Typical dopants are metals and all the rare earths e.g. Cu, Ag, Mn, Eu, Sm, Tb and Ce.

According to a tenth embodiment of the layer configuration, according to the present invention, the layer configuration further comprises a layer of an electroluminescent phosphor, wherein the electroluminescent phosphor is encapsulated with a transparent barrier layer against moisture e.g. Al_2O_3 and AlN. Such phosphors are available from Sylvania, Shinetsu polymer KK, Durel, Acheson and Toshiba. An example of coatings with such phosphors is 72X, available from Sylvania/GTE, and coatings disclosed in US 4,855,189.

According to an eleventh embodiment of the layer configuration, according to the present invention, the layer configuration further comprises a layer of an electroluminescent phosphor, wherein the electroluminescent phosphor is ZnS doped with manganese, copper or terbium or $CaGa_2S_4$ doped with cerium, e.g. the electroluminescent phosphor pastes supplied by DuPont: LUXPRINT™ type 7138J, a white phosphor; LUXPRINT™ type 7151J, a green-blue phosphor; and LUXPRINT™

type 7174J, a yellow-green phosphor; and ELECTRODAG™ EL-035A
supplied by Acheson.

According to a twelfth embodiment of the layer configuration,
according to the present invention, the layer configuration further
5 comprises a layer of an electroluminescent phosphor, wherein the
electroluminescent phosphor is a zinc sulphide phosphor doped with
manganese and encapsulated with AlN.

Dielectric layer

10

According to a thirteenth embodiment of the layer configuration,
according to the present invention, the layer configuration further
comprises a dielectric layer.

Any dielectric material may be used in the dielectric layer,
15 with yttria and barium titanate being preferred e.g. the barium
titanate paste LUXPRINT™ type 7153E high K dielectric insulator
supplied by DuPont and the barium titanate paste ELECTRODAG™ EL-040
supplied by Acheson. A positive ion exchanger may be incorporated
into the dielectric layer to capture any ions dissolving escaping
20 from the phosphor of the light-emitting layer. The amount of ion
exchanger in the dielectric layer has to be optimized so that it has
a maximum effectiveness in reducing black spots while not reducing
the initial brightness level. It is therefore preferred to add 0.5
to 50 parts by weight of ion exchanger to 100 parts by weight of the
25 total amount of resin and dielectric material in the dielectric
layer. The ion exchanger may be organic or inorganic.

Suitable inorganic ion exchangers are hydrated antimony
pentoxide powder, titanium phosphate, salts of phosphoric acid and
silicic acid and zeolite.

30

Support

According to a fourteenth embodiment of the layer configuration,
according to the present invention, the support is transparent or
35 translucent.

According to a fifteenth embodiment of the layer configuration,
according to the present invention, the support is a polymeric film,
silicon, a ceramic, an oxide, glass, polymeric film reinforced
glass, a glass/plastic laminate, a metal/plastic laminate,
40 optionally treated paper and laminated paper.

According to a sixteenth embodiment of the layer configuration,
according to the present invention, the support is provided with a

subbing layer or other adhesion promoting means to aid adhesion to the substantially transparent layer configuration.

According to a seventeenth embodiment of the layer configuration, according to the present invention, the support is a
5 transparent or translucent polymer film.

A transparent or translucent support suitable for use with the electroconductive or antistatic layers, according to the present invention, may be rigid or flexible and consist of a glass, a glass-polymer laminate, a polymer laminate, a thermoplastic polymer or a
10 duroplastic polymer. Examples of thin flexible supports are those made of a cellulose ester, cellulose triacetate, polypropylene, polycarbonate or polyester, with poly(ethylene terephthalate), poly(ethylene naphthalene-1,4-dicarboxylate), polystyrene, polyethersulphone, polycarbonate, polyacrylate, polyamide,
15 polyimides, cellulose triacetate, polyolefins and poly(vinyl chloride), optionally treated by corona discharge or glow discharge or provided with a subbing layer.

Electroluminescent devices
20

Aspects of the present invention are realized by an electroluminescent device comprising a layer configuration prepared according to the process, according to the present invention.

According to an eighteenth embodiment of the layer
25 configuration, according to the present invention, the layer configuration is an electroluminescent device.

According to a nineteenth embodiment of the layer configuration, according to the present invention, the layer configuration is a light emitting diode.
30 Thin film electroluminescent devices (ELDs) are all characterized by one (or more) electroluminescent active layer(s) sandwiched between two electrodes. Optionally a dielectric layer may also be part of the sandwich.

Thin film ELDs can be subdivided into organic and inorganic
35 based ELDs. Organic-based thin film ELDs can be subdivided into low molecular weight organic devices including oligomers (Organic Light Emitting Diodes (OLEDs)) and high molecular weight organic devices (Polymer Light Emitting Diodes (PLEDs). The inorganic ELDs on the other hand can be further subdivided into the High Voltage
40 Alternating Current (HV-AC) ELDs and the Low Voltage Direct Current (LV-DC) ELDs. The LV-DC ELDs include Powder ELDs (DC-PEL Devices or

DC-PELDs) and thin film DC-ELDs, hereinafter called Inorganic Light Emitting Diodes (ILEDs).

The basic construction of organic ELDs (PLED and OLED) comprises following layer arrangement: a transparent substrate (glass or
5 flexible plastic), a transparent conductor, e.g. Indium Tin Oxide (ITO), a hole transporting layer, a luminescent layer, and a second electrode, e.g. a Ca, Mg/Ag or Al/Li electrode. For OLEDs the hole transporting and luminescent layers are 10-50 nm thick and applied by vacuum deposition, whereas for PLEDs the hole transporting layer
10 is usually about 40 nm thick and the luminescent layer is usually about 100 nm thick and applied by spin coating or other non-vacuum coating techniques. A direct voltage of 5-10 V is applied between the electrodes and light emission results from holes and electrons being injected from the positive and negative electrodes
15 respectively combining in the luminescent layer thereby producing the energy to excite the luminescent species to emit light.

In OLEDs the hole transporting layer and electroluminescent layer consist of low molecular organic compounds e.g. N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine can be used as the hole transporter and
20 aluminium (III) 8-hydroxyquinoline complex, polyaromatics (anthracene, perylene and stilbene derivatives) and polyheteroaromatics (oxazoles, oxadiazoles, thiazoles etc.) can be used as electroluminescent compounds. In PLEDs electroluminescent compounds that can be used are polymers like the non-conjugated
25 poly(N-vinylcarbazole) derivatives (PVK) or conjugated polymers like poly(p-phenylene vinylenes) (PPV), polyfluorenes, poly(3-alkylthiophene) and poly(p-phenylene ethynylenes).

Low voltage DC PEL Devices generally comprise a transparent substrate, a transparent conductor (ITO), a doped ZnS phosphor layer
30 (20μm), and a top electrode of evaporated aluminium. The phosphor layer is applied by means of the doctor blade technique or screen printing on an ITO conducting layer. Then an aluminium electrode is applied by evaporation. Upon applying a direct current voltage of several volts (ITO positive), holes start moving towards the
35 aluminium electrode, thereby creating an insulating region (about 1 μm in thickness) next to the ITO layer within one minute or so. This results in a current drop which is associated with the onset of light emission. This process has been called the forming process. In the thin high resistive phosphor layer thereby formed, high electric
40 fields occur and electroluminescence is already possible at low voltages (typically between 10 and 30 V).

In hybrid LEDs, inorganic emitting so-called quantum dots are used in combination with organic polymers with charge transporting properties and in some cases also emitting properties. Hybrid LEDs with CdSe nano-particles have been reported by Colvin et al. [see Nature, volume 370, pages 354-357, (1994)], Dabbousi et al. [see Appl. Phys. Lett., volume 66, pages 1316-1318 (1995), and Gao et al. [see J. Phys. Chem. B, volume 102, pages 4096-4103 (1998)], herein incorporated by reference.

Light emitting devices with ZnS:Cu nano-crystals and a non-semiconducting polymer have been reported by Huang et al. [see Appl. Phys. Lett., volume 70, pages 2335-2337 (1997)] and Que et al. [see Appl. Phys. Lett., volume 73, pages 2727-2729 (1998), herein incorporated by reference, with turn on voltages below 5 V.

Photovoltaic devices

Aspects of the present invention are realized by a photovoltaic device comprising a layer configuration prepared according to the process, according to the present invention.

According to a twentieth embodiment of the layer configuration, according to the present invention, the layer configuration is a photovoltaic device.

According to a twenty-first embodiment of the layer configuration, according to the present invention, the layer configuration further comprises at least one photovoltaic layer. The photovoltaic layer may be organic layer, a hybrid inorganic and organic layer or an inorganic layer.

According to a twenty-second embodiment of the layer configuration, according to the present invention, the layer configuration is a solar cell.

Photovoltaic devices incorporating the layer configuration, according to the present invention, can be of two types: the regenerative type which converts light into electrical power leaving no net chemical change behind in which current-carrying electrons are transported to the anode and the external circuit and the holes are transported to the cathode where they are oxidized by the electrons from the external circuit and the photosynthetic type in which there are two redox systems one reacting with the holes at the surface of the semiconductor electrode and one reacting with the electrons entering the counter-electrode, for example, water is oxidized to oxygen at the semiconductor photoanode and reduced to hydrogen at the cathode. In the case of the regenerative type of

photovoltaic cell, as exemplified by the Graetzel cell, the electron transporting medium may be a nano-porous metal oxide semiconductor with a band-gap of greater than 2.9 eV, such as titanium dioxide, niobium(V) oxide, tantalum(V) oxide and zinc oxide, the hole

5 transporting medium may be a liquid electrolyte supporting a redox reaction, a gel electrolyte supporting a redox reaction, an organic hole transporting material, which may be a low molecular weight material such as 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)9,9'-spirobifluorene (OMeTAD) or triphenylamine compounds or a

10 polymer such as PPV-derivatives, poly(N-vinylcarbazole) etc., or inorganic semiconductors such as CuI, CuSCN etc. The charge transporting process can be ionic as in the case of a liquid electrolyte or gel electrolyte or electronic as in the case of organic or inorganic hole transporting materials.

15   Such regenerative photovoltaic devices can have a variety of internal structures in conformity with the end use. Conceivable forms are roughly divided into two types: structures which receive light from both sides and those which receive light from one side. An example of the former is a structure made up of a transparently

20 conductive layer e.g. an ITO-layer or a PEDOT/PSS-containing layer and a transparent counter electrode electrically conductive layer e.g. an ITO-layer or a PEDOT/PSS-containing layer having interposed therebetween a photosensitive layer and a charge transporting layer. Such devices preferably have their sides sealed with a polymer, an

25 adhesive or other means to prevent deterioration or volatilization of the inside substances. The external circuit connected to the electrically-conductive substrate and the counter electrode via the respective leads is well-known.

        Alternatively the spectrally sensitized nano-porous metal oxide,
30 according to the present invention, can be incorporated in hybrid photovoltaic compositions such as described in 1991 by Graetzel et al. in Nature, volume 353, pages 737-740, in 1998 by U. Bach et al. [see Nature, volume 395, pages 583-585 (1998)] and in 2002 by W. U. Huynh et al. [see Science, volume 295, pages 2425-2427 (2002)]. In

35 all these cases, at least one of the components (light absorber, electron transporter or hole transporter) is inorganic (e.g. nano-TiO_2 as electron transporter, CdSe as light absorber and electron transporter) and at least one of the components is organic (e.g. triphenylamine as hole transporter or poly(3-hexylthiophene) as hole

40 transporter).

24

Transistors

Aspects of the present invention are realized by a transistor comprising a layer configuration prepared according to the process, according to the present invention.
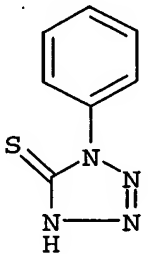
According to a twenty-third embodiment of the layer configuration, according to the present invention, the layer configuration further comprises a layer with one or more of the electron transporting or hole transporting components described above, but within such a configuration that it can be used as a transistor. The semiconductor can be n-type, p-type or both (ambipolar transistor) and can be either organic or inorganic.
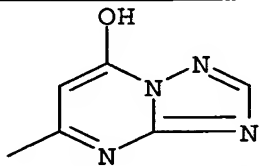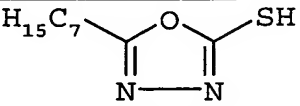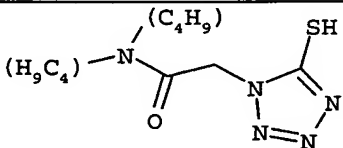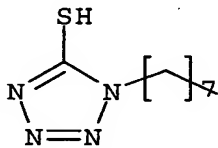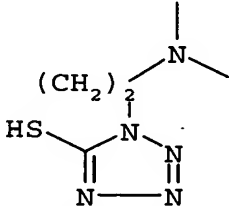
Industrial application

Layer configurations comprising at least a first layer comprising an intrinsically conductive polymer and a second layer consisting of a non-continuous layer of conductive silver can be used in a wide range of electronic devices such as photovoltaic devices, solar cells, batteries, capacitors, light emitting diodes, organic and inorganic electroluminescent devices, smart windows, electrochromic devices, sensors for organic and bio-organic materials and field effect transistors [see also chapter 10 of the Handbook of Oligo- and Polythiophenes, Edited by D. Fichou, Wiley-VCH, Weinheim (1999)].

The invention is illustrated hereinafter by way of EXAMPLES. The percentages and ratios given in these examples are by weight unless otherwise indicated.

Ingredients used in the comparative experiments of EXAMPLE 2:

	Structural formula	
STAB01		1-phenyl-5-mercapto-tetrazole
STAB02		sodium tartrate
STAB03		thiourea

STAB04	Na₂S	sodium sulphide
STAB05		5-methyl-s-triazolo[1,5-a]pyrimidin-7-ol
STAB06		
STAB07		
STAB08		
STAB09		

EXAMPLE 1

Conductive Ag-pattern made by development of a silver halide
emulsion with an outermost PEDOT/PSS layer

Preparation of the photographic emulsion layer:

A photographic AgCl(63.29%)Br(36.31%)I(0.40%) emulsion in gelatine
was prepared using the double jet precipitation technique. The
average silver halide particle size was 300 nm. After the
precipitation step the emulsion was washed and different amounts of
gelatine were added to yield the gelatine to $AgNO_3$ (g/g) ratio's
listed in Table 1. This emulsion was chemically ripened and was
spectrally sensitized to render the emulsion sensitive to He/Ne
laser exposure. The emulsion was coated on a subbed 100µm thick
polyethylene terephthalate support to a coverage equivalent to 5 g
$AgNO_3$ per square meter. This is photographic material A.

Surface resistance measurements:

The surface resistance measurements were carried out as follows:
the layer electrode configurations were cut into strips 3.5 cm in
width to ensure perfect positioning of the electrode material;
parallel copper electrodes each 35 mm long, 3 mm wide and 35 mm
apart, capable of forming line contacts and mounted on a TEFLON™
insulator were brought into contact with the outermost conductive
layer of the strip giving a contacting area of 3.5×3.5 cm^2, a
constant contact force being ensured by placing a 4 kg weight on the
TEFLON™ mounting; and the surface resistance was then directly
measured using a Fluke-77 III Multimeter.

The surface resistances determined for different gelatine to
AgNO$_3$ ratios after full area exposure with an AGFA-GEVAERT™ AVANTRA
recorder and subsequent development in the AGFA-GEVAERT™ IPDplus
developer, fixed in an AGFA-GEVAERT™ G333 fixer and finally rinsed
in water are given in Table 1.

Table 1:

Material	Gelatine/AgNO$_3$ (g/g)	Surface resistance [Ω/square]
A1	0.40	$> 10^7$
A2	0.30	60
A3	0.20	20
A4	0.18	15
A5	0.14	10

Table 1 shows that the lower the gelatine content the lower the
surface resistance. This can be explained by developed silver
particles touching each other at low gelatine contents and hence
creating a conductive path. Material A5 yields the highest surface
conductance, but for convenience reasons, material A4 was used in
the further examples.

Preparation of the PEDOT/PSS dispersion:

EP-A 686662 (US 5,766,515) discloses in the example the preparation
of a 1.2% PEDOT/PSS dispersion in water. 15 mL of a 2% solution of
ZONYL™ FSO100 in water, 1.25 g of Z6040, a silane from DOW CORNING
and 25 g of diethyleneglycol were added to 106 g of this dispersion
to give the PEDOT/PSS dispersion used in the following EXAMPLES.

Preparation of double layer electrode configuration of Material B:

The unexposed Material A4 was coated with the PEDOT/PSS dispersion to a wet thickness of 50 μm and then dried for 20 minutes at 120°C.
5 The surface resistivity of the PEDOT/PSS layer was about 500 Ω/square. The resulting layer configuration was then exposed with the AGFA-GEVAERT™ AVANTRA recorder with the patterns shown in Figure 1 and developed as described above.

10 Preparation of double layer electrode configuration of Material C:

The PEDOT/PSS-dispersion was coated on the processed material A4 to a wet thickness of 50 μm and then dried for 20 minutes at 120°C, thereby producing Material C. The surface resistance of the
15 PEDOT/PSS layer was about 500 Ω/square in the non-exposed regions material A4.

Evaluation of Materials A4 (exposed and developed), B and C:

20   The surface resistances determined as described above are given in Table 2 for the double layer electrode configurations with a developed silver pattern coated with a PEDOT/PSS outermost layer of Materials B and C, together with that for the exposed and developed Material A4 without an PEDOT/PSS outermost layer as a control
25 material.
      The optical density of the layer configurations were determined in transmission using a MacBeth™ TD924 densitometer with a visible filter for layer configurations without photographic treatment, in pattern type (d) in which no silver was developed and in pattern (a)
30 in which silver was developed over the whole 3 cm x 3 cm area without deducting the density of the support. These measurements were then used to calculate the overall optical density for patterns (b) and (c). The optical density results are also given in Table 2.
35   From Table 2 it can be concluded that (1) it is possible to expose the PEDOT/PSS layer to the IPDplus developer and G333 fixer with only minor losses in surface conductivity and (2) the Ag-lines increase the "apparent" surface conductivity. Due to the measurement set-up, only the PEDOT/PSS is contacted (top-layer). From the high
40 surface conductivity values, the PEDOT/PSS-Ag contact appears to be Ohmic in nature.

If the PEDOT/PSS coating is applied before the exposure and
development, it functions as a protective coating and therefore
material B is in most cases preferred over material C, because this
allows for automatic handling (exposure and development) without any
danger of damaging the material.

Table 2:

Control material	Description	Pattern used from Fig 1		trans- mission O.D.	Surface resistance [Ω/square]
		type	description		
A4	Without any photographic treatment	-	-	-	> 2 x 10^7
A4	After exposure and development	a	Solid area	3.70	15
A4	After exposure and development	b	1 mm lines, 10 mm spacing	0.35*	100
A4	After exposure and development	c	150 μm lines, 5 mm spacing	0.13*	340
A4	After exposure and development	d	No Ag developed	0.03	> 2 x 10^7
Invention material					
B	Without any photographic treatment	-	-	-	450
B	After exposure and development	a	Solid area	3.90	13
B	After exposure and development	b	1 mm lines, 10 mm spacing	0.48*	150
B	After exposure and development	c	150 μm lines, 5 mm spacing	0.25*	360
B	After exposure and development	d	No Ag developed	0.15	470
C	Without any photographic treatment	-	-	-	500
C	After exposure and development	a	Solid area	3.80	14
C	After exposure and development	b	1 mm lines, 10 mm spacing	0.45*	108
C	After exposure and development	c	150 μm lines, 5 mm spacing	0.22*	360
C	After exposure and development	d	No Ag developed	0.11	720

* calculated value

EXAMPLE 2

Conductive Ag-pattern made by DTR with conductive PEDOT/PSS on top

5 Preparation of the control material, Material D:

The preparation of the physical development nuclei (PdS) is described in the example of EP-A 0769 723. From this example solutions A1, B1 and C1 were used to prepare the nuclei. To 1000 mL
10 of this PdS dispersion 10 g of a 10 g/L water solution of Aerosol™ OT from American Cyanamid and 5 g of a 50 g/L solution of perfluorcaprylamide-polyglycol were added. This dispersion was then coated to a wet layer thickness of 13.5 μm on a poly(ethylene terephthalate) support with a 4 μm thick gelatine subbing layer and
15 then dried for 60 minutes at 25°C. This is material D.

Preparation of material E:

The above-described PEDOT/PSS dispersion was used to coat material D
20 to a wet thickness of 40 μm and was then dried for 15 minutes at 100°C, thereby producing material E.

Preparation of the transfer emulsion layer:

25 The preparation of the silver chlorobromide emulsion and the preparation of the transfer emulsion layer was as disclosed in EP-A 769 723 except that the coverage of silver halide applied was equivalent to 1.25 g/m^2 of AgNO$_3$ instead of 2 g/m^2 thereof.

30 Exposure and development of Materials D and E:

The transfer emulsion layer was exposed image-wise as shown in Figure 1 and processed in contact with the receiver (Material D and material E) at 25°C for 10s with a AGFA-GEVAERT™ CP297 developer
35 solution.

Preparation of the double layer electrode configuration:

Processed material D was coated with the above-described PEDOT/PSS-
40 dispersion to a wet-layer thickness of 50 μm and then dried for 20 minutes at 120°C. The surface resistivity of the PEDOT/PSS layer was

about 500 Ohm/Sq in the non-exposed areas of material D. Material F
was thereby prepared.

Evaluation of materials D, E and F:

The surface resistances and optical densities (complete
material) after exposure and development according to the patterns
shown in Figure 1 are given in Table 3.

Table 3:

Control material	Description	Pattern used from Fig 1		trans- mission O.D.	Surface resistance [Ω/square]
		type	description		
D	Without any photographic treatment	-	-	0.04	$> 2 \times 10^7$
D	After transfer reaction	a	Solid area	2.50	2.1
D	After transfer reaction	b	1 mm lines, 10 mm spacing	0.35*	16
D	After transfer reaction	c	150 μm lines, 5 mm spacing	0.20*	109
D	After transfer reaction	d	No Ag developed	0.04	$> 2 \times 10^7$
Invention material					
E	Without any photographic treatment	-	-	0.09	500
E	After transfer reaction	a	Solid area	2.30	5.2
E	After transfer reaction	b	1 mm lines, 10 mm spacing	0.33*	37
E	After transfer reaction	c	150 μm lines, 5 mm spacing	0.19*	165
E	After transfer reaction	d	No Ag developed	0.07	800
F	Without any photographic treatment	-	-	0.10	650
F	After transfer reaction	a	Solid area	2.50	2.3
F	After transfer reaction	b	1 mm lines, 10 mm spacing	0.35*	18
F	After transfer reaction	c	150 μm lines, 5 mm spacing	0.20*	120
F	After transfer reaction	d	No Ag developed	0.09	750

* calculated values

From Table 3 it can be concluded that it is possible to (1)
transfer Ag-salts trough the PEDOT/PSS layer, (2) expose the
PEDOT/PSS layer to the AGFA-GEVAERT™ CP297 developer with only a

minor loss in surface conductivity without affecting the optical transparency and (3) the Ag-lines increase the "apparent" surface conductivity significantly.

Only the outermost PEDOT/PSS layer is contacted in the surface resistance measurements. From the high surface conductivity values, the PEDOT/PSS-Ag contact appears to be Ohmic in nature. If the PEDOT/PSS coating is applied before the exposure and development, it functions as a protective coating and therefore material E is in most cases preferred over material F, because this allows for automatic handling (exposure and development) without any danger of damaging the material.

Improving of the surface conductance of the Ag°-image by etching in presence of halide ions followed by a chemical development

Due to the fact that the DTR process is a physical development, the resulting Ag°-particles are smooth and rounded. Chemical development, which is more explosive, results in a higher degree of particle overlap and particle touching and hence will result in patterns with higher conductivity. However, this type of development does not take place in a DTR process. In order to improve the surface conductance of a Ag°-image obtained by the DTR-process, the conductive Ag°-pattern obtained by the DTR process was further processed by first treating it with an etching solution containing an oxidizer and halide ions (thereby partially oxidizing the Ag° to Ag$^+$ which is present as AgCl, AgBr or AgBrCl depending upon the halides used), then developing with a Graphic developer which brought about explosive or chemical development of the newly formed silver halide crystals and finally fixing and washing. When this process was applied to freshly produced processed material D with pattern "a" using AGFA-GEVAERT™ IPDplus developer and AGFA-GEVAERT™ G333 fixer an up to 18% decrease in surface resistance (= 18% increase in surface conductance) was realized. The etching bath compositions and etching times are given in Table 4.

Table 4:

Bath nr	Bath composition				Etching time (s)
	$KMnO_4$ [g/L]	$K_4Fe(CN)_6$ [g/L]	KCl [g/L]	KBr [g/L]	
1	-	1	-	10	30
2	-	1	10	-	30
3	-	0.1	-	10	30
4	-	0.1	10	-	30
5	0.01	-	-	10	30
6	0.01	-	10	-	30
7	0.005	-	-	10	30
8	0.005	-	10	-	30
9	0.01	-	5	-	120
10	0.01	-	10	-	120
11	0.01	-	25	-	120
12	0.01	-	-	5	30
13	0.01	-	-	10	30
14	0.01	-	-	25	30
15	0.01	-	2.5	2.5	30
16	0.01	-	5	5	30
17	0.01	-	10	10	30
18	0.01	-	2.5	2.5	60
19	0.01	-	5	5	60
20	0.01	-	10	10	60
21	0.01	-	2.5	2.5	120
22	0.01	-	5	5	120
23	0.01	-	10	10	120

The optical density was measured with a MacBeth™ densitometer
TD904 with a visible filter. The surface resistances and optical
densities obtained are given in Table 5.

From Table 5 it is clear that the kind and amount of oxidising
agent used is very important: an oxidising agent which is too strong
or too concentrated will destroy the conductive pattern too rapidly.
If the oxidising agent is too weak or too dilute, almost nothing
will happen. Also the amount and kind of halide ions is important as
can be seen from Table 5.

Table 5:

Bath nr	D_max		Surface resistance [Ω/square]		
	before etching	etching after + development	before etching	after etching + development	% change
1	2.84	2.75	3.7	3.5	-7
2	2.90	2.88	2.7	2.9	+5
3	2.92	2.87	2.7	3.0	+10
4	3.00	2.89	3.0	2.9	-5
5	2.48	2.27	2.5	6.4	+156
6	2.69	2.61	2.5	2.4	-4
7	2.52	2.65	2.5	2.7	+8
8	2.76	2.52	2.5	2.3	-8
9	2.49	2.36	2.7	2.7	0
10	2.50	2.38	3.0	2.6	**-13**
11	2.48	2.44	2.8	2.8	0
12	2.84	2.80	2.6	2.4	-8
13	2.72	2.63	3.2	3.3	+3
14	2.55	2.48	2.3	2.3	0
15	2.45	2.31	3.4	3.0	**-12**
16	2.47	2.36	3.1	2.8	**-10**
17	2.46	2.23	3.3	3.0	-9
18	2.50	2.33	3.3	3.0	-9
19	2.38	2.23	3.2	2.8	**-13**
20	2.48	2.32	3.4	2.8	**-18**
21	2.47	2.33	3.3	3.0	-9
22	2.52	2.37	3.2	2.8	**-13**
23	2.48	2.35	3.2	2.7	**-16**

Recovery of the PEDOT/PSS conductivity after IPDplus
processing by means of re-oxidizing the PEDOT/PSS layer

The surface resistance of the outermost PEDOT/PSS-layer in Material B was not substantially increased upon 30s contact with the AGFA-GEVAERT™ IPDplus developer, but the surface resistance of the PEDOT/PSS-layer of the AGFA-GEVAERT™ ORGACON film increased from 500 Ω/square to ~3000 Ω/square upon 30s contact therewith. It has been found, however, that the original surface resistance can be largely recovered by treatment with solutions of particular oxidizing agents for 30 s at 25°C. The compositions of the solutions of oxidizing agent used and the surface resistances results obtained before contact with the IPDplus developer, after contact with the IPDplus developer and after subsequent contact with the particular oxidizing solution are given in Table 6.

Table 6:

solution of oxidising agent in water (% by weight)	Surface resistance [Ω/square]		
	before processing in IPDplus (35°C & 30s)	after processing in IPDplus (35°C & 30s)	after processing in oxidising agent solution
$FeCl_3$ (0.1%)	503	3270	1608
$FeCl_3$ (2%)	452	3015	1440
H_2O_2 (2%)	466	3450	2963
H_2O_2 (10%)	485	3270	2238
$K_3Fe(CN)_6$ (0.1%)	459	3075	1722
$K_3Fe(CN)_6$ (2%)	549	3600	1607
Dimethylsulfoxide(0.1%)	513	2385	1793
HNO_3 (0.1%)	449	2160	1299
$Na_2S_2O_8$ (2%)	432	2130	1400
Succinic acid (0.1%)	440	2400	1781
Succinic acid (2%)	543	2835	1514

5 The best results were realized with aqueous solutions of $Na_2S_2O_8$ and $FeCl_3$ with which the surface resistance after contact with the IPDplus developer decreased by a factor of 2 to ~1500 Ω/square, but this was still a factor of 3 above the surface resistance of the ORGACON film prior to contact with IPDplus developer.

10

EXAMPLE 3

Conductive Ag-pattern made by Diffusion Transfer Reaction with patterned conductive PEDOT/PSS on top.

15

Sometimes it is necessarily to have a patterned transparent conductive layer on top of a high conductive metallic pattern (e.g. EXAMPLE 5). This can be done by applying patterned the PEDOT/PSS on top of the emulsion layer (as described in example 1) prior to
20 exposure and development or applying patterned PEDOT/PSS on top of the nuclei layer (as described in example 2) prior to the diffusion transfer process. Analogously, as was described in examples 1 and 2 (comparison), the patterned PEDOT/PSS can also be applied after the formation of the Ag-pattern. The patterning of the PEDOT/PSS can be
25 subtractive by destroying its conductivity (e.g. EP-A 1054414, EP-A 1079397) or additive by using printing techniques like flexographic

printing, screen printing, tampon printing, off set printing and ink jet printing.

Preparation of the control material, Material G:

To 1000 mL of the above described PdS dispersion 10 mL of a 50 g/L in water solution of Antarox CO630 from GAF was added. This dispersion was then coated to a wet-layer thickness of 13.5 μm on a PET substrate with a 2 μm thick gelatine subbing layer and was then dried for 60 minutes at 25°C to give Material G.

Preparation of the screen print paste of PEDOT/PSS:

The screen print paste was prepared by adding 3.47 kg of 1,2-propandiol and 0.38 kg of diethylene glycol to 2.56 kg of a 1.2% by weight dispersion of PEDOT/PSS with a weight ratio of PEDOT to PSS of 1:2.4 in a reactor, then distilling off 1.5 L of water by heating with an oil bath at 62°C under stirring at a vacuum which varied between 31 and 55 mbar over a period of 234 minutes, cooling the resulting mixture to 20°C and then distilling off a further 0.49 L of water by heating with an oil bath at 60.5°C with stirring at a vacuum which varied between 24 and 26 mbar over a period of 287 minutes. The water content in the 3.8 kg of paste produced, as determined by the Karl Fischer method, was 3.9% by weight.

To 297 g of the obtained paste 1.5 g of 2-glycidoxypropyl-trimethoxysilane, 0.75 g of ZONYL™ FSO (ZONYL™ FSO is a 50% by wt solution of ZONYL™ FSO100 a mixture of 50% by wt of water and 50% by wt of ethylene glycol) and 0.75 g of silicone antifoam agent X50860A was added to give a screen printing paste.

Preparation of Material H:

The screen printing paste was silk screen printed with a manual press and a P120 screen onto material G to cover the final images shown in Figure 1 thereby giving Material H.

Exposure and development of Materials G and H:

The transfer emulsion layer was exposed image-wise as shown in Figure 1 and processed in contact with the receiver (Material G and Material H) at 25°C for 10s with an AGFA-GEVAERT™ CP297 developer solution.

Preparation of double layer electrode configuration of Material I:

The screen printing paste was silk screen printed with a manual
5 press and a P120 screen onto the processed material G so as to cover
the image as shown in Figure 1, thereby producing Material I.

Evaluation of Materials G, H and I:

10 The surface resistances and optical densities (complete material)
after exposure and development according to the pattern of Figure 1
are given in Table 7.

Table 7:

15

Control material	Description	Pattern used from Fig 1		trans-mission O.D.	Surface resistance [Ω/square]
		type	description		
G	Without any photographic treatment	-	-	0.03	$> 2 \times 10^7$
G	After transfer reaction	a	Solid area	2.35	2.2
G	After transfer reaction	b	1 mm lines, 10 mm spacing	0.24*	18
G	After transfer reaction	c	150 μm lines, 5 mm spacing	0.10*	140
G	After transfer reaction	d	no Ag developed	0.03	$> 2 \times 10^7$
Invention material					
H	Without photographic treatment	-	-	0.10	1500
H	After transfer reaction	a	Solid area	2.10	8.5
H	After transfer reaction	b	1 mm lines, 10 mm spacing	0.28*	225
H	After transfer reaction	c	150 μm lines, 5 mm spacing	0.16*	2200
H	After transfer reaction	d	No Ag developed	0.12	18000
I	Without any photographic treatment	-	-	0.13	1250
I	After transfer reaction	a	Solid area	2.38	4.4
I	After transfer reaction	b	1 mm lines, 10 mm spacing	0.35*	30
I	After transfer reaction	c	150 μm lines, 5 mm spacing	0.20*	100
I	After transfer reaction	d	No Ag developed	0.09	1250

* calculated values

The results in Table 7 show that it is feasible to construct a double layer electrode by this method, although the surface resistance of the PEDOT/PSS screen print paste was adversely
5 affected by the AGFA-GEVAERT™ CP297 developing solution, the surface restistance increasing from 1500 Ω/square to 18000 Ω/square.

EXAMPLE 4

10 Conductive PEDOT/PSS with conductive Ag-pattern made by
Diffusion Transfer Reaction on top.

Preparation of the control material, Material J:

15 The above-described PEDOT/PSS dispersion was used to coat a polyethylene terephthalate support with a 4 μm gelatine subbing layer to a wet thickness of 40 μm and was then dried for 15 minutes at 100°C, thereby producing material J.

20 Preparation of Material K:

To 1000 mL of the above described PdS dispersion 10 g of a 10 g/L water solution of Aerosol OT from American Cyanamid and 5 g of a 50 g/L solution of perfluorcaprylamidpolyglycol were added. This
25 dispersion was then coated with a wet layer thickness of 13.5 μm on material J and then dried for 60 minutes at 25°C. This is material K.

Exposure and development of Material K:
30
The transfer emulsion layer was exposed image-wise as shown in Figure 1 and processed in contact with the receiver (Material K) at 25°C for 10s with the AGFA-GEVAERT™ CP297 developer solution. The surface resistances and optical densities (complete material) after
35 exposure and development according to the pattern of Figure 1 are given in Table 8.
Table 8 demonstrates the feasibility of a double layer electrode configuration with a Ag-conductive pattern on top of a conductive PEDOT/PSS-layer. The measured value of surface resistivity of the
40 untreated material K is 5000 Ω/square instead of 500 Ω/square. It is also not > 20 MΩ/square. This indicates a slight mixing of the layers and/or inhomogeneities in the PdS-layer. It is clear from

the above description that the nuclei layer can also be applied in a patterned way.

Table 8:

Control material	Description	Pattern used from Fig 1		trans-mission O.D.	Surface resistance [Ω/square]
		type	description		
J	Without any photographic treatment	-	-	0.04	500
J	After dipping 10 s in AGFA-GEVAERT™ CP297 developer	-	-	0.04	620
Invention material					
K	Without any photographic treatment	-	-	0.06	5000
K	After transfer reaction	a	Solid area	2.20	2.9
K	After transfer reaction	b	1 mm lines, 10 mm spacing	0.25*	33
K	After transfer reaction	c	150 μm lines, 5 mm spacing	0.12*	95
K	After transfer reaction	d	No Ag developed	0.07	1300

* calculated values

EXAMPLE 5

Application of a conductive Ag-pattern coated with a patterned conductive PEDOT/PSS in the production of thin film solar cells

Figure 2 shows side (upper) and top (lower) views of a sequential process for building up a module with a separate photovoltaic cell, two serially connected photovoltaic cells and three serially connected photovoltaic cells using a six step process in which:

A = a subbed support
B = a gelatin layer
C = a palladium sulfide nucleation layer
D = a conductive silver pattern
E = a highly conductive PEDOT/PSS-layer
F = a shunt resistance hindering layer
G = a photovoltaic blend

H = a lithium fluoride/aluminium electrode

In step 1 in which the subbed surface of a subbed poly(ethylene terephthalate) film A [the subbing layer represented by hatching] is coated with a gelatin layer B; step 2 in which a palladium sulfide nucleation layer C is applied to the gelatin layer B; step 3 in which a diffusion transfer process is carried out in which a conductive silver pattern D is produced; step 4 in which the conductive silver pattern D is coated with a highly conductive PEDOT/PSS-layer E by e.g. screen printing, and optionally additionally with a shunt resistance hindering layer F, e.g. a PEDOT/PSS layer or a PEDOT-S/polycationic or polyanionic polymer with a higher surface resistance; step 5 in which layer E or F is coated with a photovoltaic blend, e.g. a blend of MDMO-PPV/PCBM G, by e.g. curtain coating, spincoating or screen printing; and step 6 in which layer G is coated with a non-continuous lithium fluoride/aluminium layer forming a top electrode H.

This figure shows a way of using the multilayer configuration in the construction of a thin film solar cell module e.g. solar cells based on the bulk heterojunction principle. A double layer electrode (Ag-pattern - PEDOT/PSS) can be constructed by using the method described in EXAMPLE 2. This makes feasible the construction of cells with larger areas, because the charge will be collected in the conductive Ag-network.

EXAMPLE 6

Conceptual experiments were carried out with a recorder film with a gelatine to silver ratio of 0.014. Exposed areas of 1 x 3 cm^2 as electrodes with a separation of 40 μm gave conducting silver patterns upon processing by conventional graphic processing. The resulting electrode pattern had a surface resistance of 50 to 100 ohm/square.

These electrodes were conditioned for 3 days at 35°C and a relative humidity of 80%. The aqueous solutions used for treating the electrodes prior to applying a potential of 100 V between neighbouring electrodes are listed in Table 9.

Table 9:

Solution nr.	Solution		
	active ingredient	conc.(%)	solvent
1	STAB01 (1-phenyl-5-mercapto-tetrazole)	1.0	water*
2	STAB01	0.1	water*
3	STAB01 + Antarox™ CO 630#	1.0 + 0.5	water
4	STAB01 + Antarox™ CO 630#	0.1 + 0.5	water
5	STAB02 (sodium tartrate)	10	water
6	STAB02 (sodium tartrate)	1	water
7	STAB03 (thiourea)	10	water
8	STAB03 (thiourea)	1	water
9	STAB04 (sodium sulphide)	10	water
10	STAB04 (sodium sulphide)	1	water
11	STAB05 (5-methyl-s-triazolo[1,5-a]pyrimidin-7-ol)	4.25	water
12	STAB05	0.425	water
13	STAB05	1.7×10^{-2}	water
14	STAB05	1.7×10^{-4}	water
15	STAB05	1.7×10^{-5}	water
16	STAB05	1.7×10^{-6}	water
17	STAB06	0.5	water
18	STAB06	0.05	water
19	STAB06	0.005	water
20	STAB07	0.5	water
21	STAB07	0.05	water
22	STAB07	0.005	water
23	STAB08	0.5	water
24	STAB08	0.05	water
25	STAB08	0.005	water
26	STAB09	0.5	water
27	STAB09	0.05	water
28	STAB09	0.005	water
29	PMT01	0.1	ethanol
30	PMT01	0.004	ethanol
31	PMT01	4×10^{-5}	ethanol
32	PMT01	4×10^{-6}	ethanol
33	PMT02	0.5	water
34	PMT02	0.05	water
35	PMT02	0.005	water
36	PMT03	0.5	water
37	PMT03	0.05	water
38	PMT03	0.005	water
39	PMT04	0.5	ethanol
40	PMT04	0.05	ethanol

41	PMT04	0.005	ethanol
42	PMT05	0.5	water
43	PMT05	0.05	water
44	PMT05	0.005	water
45	PMT06	0.05	water
46	PMT06	0.005	water
47	PMT07	0.05	water
48	PMT07	0.005	water
49	PMT08	0.5	water
50	PMT08	0.05	water
51	PMT08	0.005	water
52	PMT09	0.5	water
53	PMT09	0.05	water
54	PMT09	0.005	water
55	PMT10	0.5	water
56	PMT10	0.05	water
57	PMT11	0.05	water
58	PMT11	0.005	water
59	PMT12	0.05	water
60	PMT12	0.005	water
61	PMT13	0.05	water
62	PMT13	0.005	water
63	PMT14	0.05	water
64	PMT14	0.005	water

\# a nonyl-phenyl-oxy- polyethyleneglycol(EO 9.5), from GAF

After treatment of the electrodes by dipping in the solution for 1 minute at 25°C, a potential of 100 V was applied between neighbouring electrodes for 20 minutes. The result was viewed under a microscope and recorded photographically. The gap between the electrodes without pretreatment and before applying a potential was determined to be 43.0 ± 0.7 μm. Tables 10 and 11 record the final gap width and general observations concerning silver dendrite formation after particular pretreatments and the subsequent application of a potential of 100 V for 20 minutes for the comparative experiments with STAB01 to STAB09 and for the invention experiments with PMT01 to PMT14 respectively.

Table 10:

Comparative experiment nr.	solution nr.	result of applying 100 V for 20 min. between electrodes	
		final width of gap [μm]	observations
1#	none	25.8 ± 1.0	front formation
2*	none	28.3 ± 1.0	front formation
3*	none	43.1 ± 1.2	dendrites, but no front formation
4	1	23.6 ± 1.8	front formation
5	2	21.5 ± 2.5	front formation
6	3	25.5 ± 2.9	front formation
7	4	41.8 ± 0.7	dendrite formation
8	5	35.5 ± 1.3	front formation but loss of electrode contact
9	6	33.6 ± 1.7	front formation
10	7	27.8 ± 1.9	front formation
11	8	26.2 ± 2.9	front formation
12	9	22.1 ± 4.1	front formation but loss of electrode contact
13	10	27.8 ± 2.7	front formation
14	11	30.4 ± 1.7	front formation
15	12	26.0 ± 1.2	front formation
16	13	21.8 ± 2.0	zones with front formation/ zones with dendrites but no front formation
17	14	23.5 ± 3.1 / 43.8 ± 0.7	zones with front formation/ zones with dendrites but no front formation
18	15	25.7 ± 2.1 / 42.4 ± 1.0	zones with front formation/ zones with dendrites but no front formation
19	16	22.6 ± 2.3	zones with front formation/ zones with dendrites but no front formation
20	17	28.6 ± 0.6	front formation
21	18	26.7 ± 0.6	front formation
22	19	43.2 ± 0.6	dendrites, but no front formation
23	20	23.4 ± 0.9	front formation
24	21	24.9 ± 1.1	front formation
25	22	24.6 ± 0.6	front formation
26	23	32.2 ± 2.3	front formation
27	24	43.3 ± 0.6	dendrites, but no front formation
28	25	42.4 ± 1.8	dendrites, but no front formation
29	26	42.7 ± 1.7	dendrites, but no front formation
30	27	43.1 ± 1.0	occasional dendrites
31	28	43.0 ± 0.4	occasional dendrites

neither conditioning nor solution pretreatment prior to application of 100 V DC

* no solution pretreatment between conditioning and application of 100 V DC

Table 11:

Invention experiment nr.	solution nr.	result of applying 100 V for 20 min. between electrodes	
		final width of gap [µm]	observations
1	29	41.9 ± 0.7	almost no dendrite formation
2	30	42.4 ± 0.7	almost no dendrite formation
3	31	41.5 ± 0.4	almost no dendrite formation
4	32	41.4 ± 1.1	occasional dendrites
5	33	29.8 ± 0.4	front formation
6	34	29.4 ± 1.4	front formation
7	35	43.1 ± 0.3	dendrites, but no front formation
8	36	42.9 ± 0.4	occasional dendrites
9	37	42.6 ± 0.7	occasional dendrites
10	38	43.3 ± 0.75	dendrites, but no front formation
11	39	42.4 ± 0.8	almost no dendrite formation
12	40	43.4 ± 0.7	occasional dendrites
13	41	42.4 ± 1.0	dendrites, but no front formation
14	42	43.9 ± 0.8	dendrites, but no front formation
15	43	43.8 ± 0.6	almost no dendrite formation
16	44	44.2 ± 0.4	almost no dendrite formation
17	45	42.9 ± 0.7	dendrites, but no front formation
18	46	43.4 ± 0.7	almost no dendrite formation
19	47	43.5 ± 1.0	occasional dendrites
20	48	43.2 ± 0.9	occasional dendrites
21	49	25.4 ± 2.3	front formation
22	50	43.4 ± 0.8	occasional dendrites
23	51	43.7 ± 0.4	almost no dendrite formation
24	52	43.3 ± 0.7	dendrites, but no front formation
25	53	42.0 ± 0.8	occasional dendrites
26	54	43.9 ± 0.5	almost no dendrite formation
27	55	24.1 ± 4.0	front formation
28	56	42.9 ± 0.9	dendrites, but no front formation
29	57	25.6 ± 3.3	front formation
30	58	43.0 ± 0.5	occasional dendrites
31	59	23.4 ± 3.0	front formation
32	60	42.8 ± 0.4	almost no dendrite formation
33	61	42.2 ± 0.6	occasional dendrites
34	62	41.9 ± 1.2	occasional dendrites
35	63	26.1 ± 2.1	front formation
36	64	41.6 ± 1.1	occasional dendrites

These results show migration of silver ions upon conditioning for 3 days at 35°C and 80% relative humidity and subsequent

application of a potential of 100 V DC for 20 minutes in the absence of pretreatment (comparative experiments 2 and 3). A comparison of the results with comparative experiments 1 and 2 show that conditioning clearly promoted silver dendrite growth as observed in
5 actual devices.

Pretreatment with an aqueous solution of sodium tartrate (STAB02) provided limited restraint as shown by the reduced growth of the silver dendrite front. Pretreatment with high concentrations of sodium sulphide (STAB04) appeared to detach the silver dendrite
10 front from the electrode. Low concentrations of 5-methyl-s-triazolo[1,5-a]pyrimidin-7-ol (STAB05) also restrained silver dendrite growth as evidenced by the break up of the silver dendrite front into clusters of silver dendrites although this was limited to particular zones.

15 All the 5-mercapto-tetrazoles investigated, with the notable exception of unsubstituted 1-phenyl-5-mercapto-tetrazole [STAB01], also exerted at least a limited restraint on the silver dendrite-formation process as could be seen by at least the appearance of a broken front formed by clusters of silver-dendrites. 1-Phenyl-5-
20 mercapto-tetrazole itself exhibited this behaviour in the presence of the surfactant Antarox™ CO 630, a non-ionic surfactant. However, substantial restraint was only observed with 1-phenyl-mercapto-tetrazole compounds with the phenyl group substituted with at least one electron accepting group such as halide, acylamino- or amido-
25 groups as shown by the compounds PMT01 to PMT14. Almost complete restraint was observed upon pretreatment with solutions 29, 30, 31, 39, 43, 44, 46, 51, 54 and 60 i.e. with PMT1, PMT05, PMT06, PMT08, PMT09 and PMT12 almost complete restraint was observed at concentrations of 1-phenyl-5-mercapto-tetrazole with phenyl groups
30 substituted with electron accepting groups of 0.005%: or lower.

Experiments in photovoltaic devices consisting of a poly(ethylene terephthalate) support/silver grid/screen-printed PEDOT-PSS-containing paste/poly{[2-methoxy-5-(2'-ethylhexoxy)-p-phenylene]vinylene}:1-(3-methoxycarbonyl)-propyl-1-1-phenyl-$(6,6)C_{61}$
35 layer/aluminium with and without PMT-1 in the silver grid layer gave the results given in Table 12 upon exposure with a halogen lamp:

Table 12:

	V_{OC} [mV]	I_{SC} [mA/cm^2]
without silver grid	830	0.7
silver grid without PMT-1	740	3.8
silver grid with PMT-1	730	5.2

The results in Table 12 show that the presence of a silver grid increased the short circuit current from 0.7 mA/cm^2 to 3.8 mA/cm^2 and reduced the open circuit voltage from 830 to 740 V. Furthermore, incorporation of PMT-1 in the silver grid layer increased the short circuit current (I_{SC}) still further to 5.2 mA/cm^2.

The present invention may include any feature or combination of features disclosed herein either implicitly or explicitly or any generalisation thereof irrespective of whether it relates to the presently claimed invention. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

Having described in detail preferred embodiments of the current invention, it will now be apparent to those skilled in the art that numerous modifications can be made therein without departing from the scope of the invention as defined in the following claims.

All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

The use of the terms "a" and "an" and "the" and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate the invention and does not pose a

limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

5   Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Of course, variations of those preferred embodiments will become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to

10 employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any

15 combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.